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54 Process for producing carbonyl compounds.

57 The invention relates to a process of producing a carbonyl compound by dehydrogenating a linear aliphatic alcohol of 1 to 6 carbon atoms in the gas phase in the presence of a solid catalyst comprising a ruthenium catalyst supported on a carrier such as zinc oxide or magnesium oxide.

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1 PROCESS FOR PRODUCING CARBONYL COMPOUNDS

2           The present invention relates to a process  
3 for producing a carbonyl compound by dehydrogenating an  
4 aliphatic alcohol. More particularly, it relates to a  
5 process for dehydrogenating an aliphatic alcohol in the  
6 gas phase using a specific solid catalyst, thereby  
7 producing a corresponding aldehyde or ketone.

8 Background of the Invention

9           Heretofore, there have been industrial proc-  
10 esses for producing acetone by dehydrogenating iso-  
11 propanol and for producing methyl ethyl ketone (MEK) by  
12 dehydrogenating sec-butanol in the presence of a solid  
13 catalyst. The solid catalyst for such processes is  
14 usually zinc oxide or a copper-zinc alloy, and they are  
15 used at high temperatures above 400°C because they are  
16 low in activity at low temperatures.

17           It is reported that the dehydrogenation of  
18 alcohols at low temperatures is effectively catalyzed  
19 by a copper-complex oxide such as CuO-ZnO, CuO-Cr<sub>2</sub>O<sub>3</sub>,  
20 and CuO-CoO-Cr<sub>2</sub>O<sub>3</sub>. However, these catalysts have a  
21 drawback in common in that they lose activity very soon  
22 and need frequent regeneration. This drawback places  
23 them under a practical disadvantage.

24           Recently an attempt has been made to de-  
25 hydrogenate an alcohol in the homogeneous liquid phase  
26 by using a complex compound of ruthenium or osmium as a  
27 catalyst. [Inorg. Chem., 16 (1), 137 (1977)] This  
28 process, however, has not yet reached the level of  
29 practical use.

30           There is known a process for producing n-  
31 decanal by dehydrogenating n-decanol using a ruthenium  
32 catalyst supported on alumina. [Gazz. Chim. Ital., 91,  
33 479 (1961)] It is reported that this process is such  
34 that the reaction does not proceed when there is no

1 oxygen in the reaction system.

2           There is also known a process for producing  
3 an alicyclic ketone by dehydrogenating an alicyclic  
4 alcohol using a ruthenium catalyst supported on a car-  
5 rier such as carbon or metal oxide although only the  
6 former is exemplified (British Patent No. 849,135).  
7 This process has the disadvantage of using essentially  
8 carbon as a carrier. The catalyst is easily deacti-  
9 vated by the carrier. Moreover, the catalyst requires  
10 a reaction temperature higher than 300°C, at which  
11 dehydration and other side reactions take place. For  
12 these reasons, this process has not been put to practi-  
13 cal use.

14           The object of the invention is to provide a  
15 catalyst that exhibits high catalytic activity at low  
16 temperatures and maintains activity for a long time in  
17 the process for producing a carbonyl compound by de-  
18 hydrogenating a lower aliphatic alcohol of 1 to 6 car-  
19 bon atoms. Applicants found that the object can be  
20 achieved by a ruthenium catalyst supported on a car-  
21 rier.

22           The gist of this invention resides in a proc-  
23 ess for producing a carbonyl compound which comprises  
24 dehydrogenating a linear aliphatic alcohol of carbon  
25 number 1 to 6 in the gas phase in the presence of a  
26 ruthenium catalyst supported on a carrier.

27           Carrier

28           The carrier used in this invention includes,  
29 for example, zinc oxide, magnesium oxide, calcium ox-  
30 ide, barium oxide, sodium carbonate, potassium car-  
31 bonate, calcium carbonate, barium carbonate, strontium  
32 carbonate, magnesium carbonate, alumina, silica alu-  
33 mina, silica, activated carbon, zeolite, and titania.  
34 Preferred among them are basic oxides such as zinc

1 oxide, magnesium oxide, calcium oxide, and barium oxide.

2 If these basic oxides are of high purity, they can be used  
3 without any problem; in the case of commercial products, however, they  
4 should preferably be incorporated with an alkaline substance  
5 such as potassium carbonate and sodium carbonate because they  
6 often contain a small amount of acidic sites derived from  
7 impurities. A preferred carrier comprises zinc oxide or  
8 magnesium oxide, optionally with a minor amount of sodium  
9 carbonate.

10 These carriers may be used individually or in  
11 combination with one another.

#### 12 Preparation of catalyst

13 The catalyst used in this invention is ruth-  
14 enium supported on the above-mentioned carrier. The  
15 supporting can be accomplished by steeping a carrier in  
16 a solution of ruthenium compound in water or organic  
17 solvent, followed by evaporation to dryness; or by  
18 steeping a carrier in a solution of ruthenium compound  
19 in water or organic solvent, and removing the solvent  
20 by filtration or decantation, followed by drying or by  
21 washing and calcination.

22 The ruthenium compound to be supported in-  
23 cludes, for example, ruthenium chloride, ruthenium  
24 bromide, ruthenium iodide, ruthenium nitrate, ammonium  
25 chlororuthenate, ammonium bromoruthenate, ammonium  
26 iodoruthenate, sodium ruthenate, potassium ruthenate,  
27 ruthenium hydroxide, ruthenium oxide, and ruthenium  
28 carbonyl.

29 The quantity of ruthenium to be supported is  
30 suitably 0.01 to 10 wt.%, preferably 0.1 to 5 wt.%.

31 Before use for the dehydrogenation reaction, the  
32 catalyst should preferably be reduced - for example by treatment  
33 with hydrogen or a reducing organic compound such as hydrazine,  
34 formalin, or methanol at room temperature to 500°C.

#### 35 Alcohol

36 The alcohol used as a feedstock in the proc-  
37 ess of this invention is a linear aliphatic alcohol of

1 carbon number 1 to 6. Examples of such an alcohol include methanol,  
2 ethanol, n-propanol, n-butanol, 2-methyl-propanol, n-pentanol, 3-  
3 methylbutanol, 2-methylbutanol, n-hexanol, 4-methylpentanol, 2-methyl-  
4 pentanol, and other primary alcohols; and 2-propanol, 2-butanol, 3-  
5 pentanol, 2-nentanol, 3-hexanol, 2-hexanol, and other secondary alcohols.

6 When dehydrogenated according to the process of  
7 this invention, the primary alcohols form their corresponding  
8 aldehydes and the secondary alcohols form their corresponding  
9 ketones. A preferred process is that in which secondary  
10 butanol is converted to MEK. 2-propanol is similarly  
11 converted to acetone.

#### 12 Method of dehydrogenation

13 The dehydrogenation is accomplished by bring-  
14 ing the alcohol into contact with the catalyst. The  
15 catalyst is placed in a fixed bed or fluidized bed; and  
16 the alcohol is supplied continuously or batchwise.

17 The reaction conditions are not specifically  
18 limited. The reaction pressure should preferably be  
19 reduced pressure or normal pressure; but reaction under  
20 pressure up to about 30 kg/cm<sup>2</sup> is permissible. The  
21 reaction temperature should be 150 to 400°C, which is  
22 high enough to keep the reaction system in the gaseous  
23 state, and preferably is 200° to 250°C. The alcohol in  
24 liquid form should be supplied at a rate (LHSV) of 0.1  
25 to 100 hr<sup>-1</sup>, preferably 0.5 to 20 hr<sup>-1</sup>.

26 If the catalyst of this invention is used, it  
27 is possible to produce a desired carbonyl compound at a  
28 sufficiently high conversion rate and selectivity at a  
29 low temperature without using a heating furnace. More-  
30 over, the catalyst maintains its high catalytic activ-  
31 ity for a long time. The catalyst is particularly  
32 suitable for converting a secondary alcohol among the  
33 above-mentioned alcohols into its corresponding ketone  
34 on an industrial scale.

35 The invention is described in more detail  
36 with reference to the following non-limiting examples

1 and referential examples, in which "%" means "wt%",  
2 unless otherwise noted.

3 Example 1

4 Zinc oxide (20 to 40 mesh) was steeped in a  
5 ruthenium chloride solution prepared by dissolving a  
6 predetermined quantity of ruthenium chloride in ace-  
7 tone. (The zinc oxide was prepared by pulverizing the  
8 commercial one available as a catalyst for alcohol  
9 dehydrogenation. It contained 3.3% of sodium carbon-  
10 ate.) After standing for 1 hour, the solution was  
11 evaporated to dryness, followed by drying in an oven at  
12 120°C for 12 hours. The resulting product was reduced  
13 with nitrogen saturated (at room temperature) with  
14 methanol at 200°C for 1 hour and then at 400°C for 1  
15 hour. Thus there was obtained a catalyst containing 1%  
16 of ruthenium.

17 2.5 cm<sup>3</sup> of this catalyst was diluted with 7.5  
18 cm<sup>3</sup> of quartz chips and the diluted catalyst was intro-  
19 duced into a stainless steel reactor tube, 18 mm in  
20 inside diameter. 2-Butanol was passed through the  
21 reactor tube for dehydrogenation under the conditions  
22 and with the results shown in Table 1.

23 Comparative Example 1

24 Dehydrogenation of alcohol was carried out in  
25 the same way as in Example 1, except that the zinc  
26 oxide powder used as the carrier was used as a catalyst  
27 as such. The results are shown in Table 1.

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Table 1

2	3	4	5	Reaction conditions *		MEK yield (mol%)**		
				Temp. (°C)	LHSV (hr <sup>-1</sup> )	After 2 hr	After 30 hr	After 150 hr
6	Example 1	Ru/ZnO	250	8	23	23	23	
7	Compar. Example 1	ZnO	250	2	2	2	-	
8	Compar. Example 2	CuO-ZnO	200	40	24	4	-	
9	Compar. Example 3	CuO/diatomaceous earth	200	40	25	6	-	
10	-do.-	-do.-	250	40	43	14	-	

11 Note: \*Reaction pressure was 10 kg/cm<sup>2</sup>G in all the cases.

12 \*\*Selectivity to MEK (methyl ethyl ketone) was

13 higher than 99 mol %.

1    Comparative Example 2

2            Dehydrogenation of alcohol was carried out in  
3    the same way as in Example 1, except that the catalyst  
4    was replaced by a commercial copper oxide-zinc oxide  
5    catalyst for alcohol dehydrogenation (CuO: 50%, ZnO:  
6    45%, specific surface area: 38.0 m<sup>2</sup>/g) which had been  
7    crushed to 20 to 40 mesh prior to use. The results are  
8    shown in Table 1.

9    Comparative Example 3

10           Dehydrogenation of alcohol was carried out in  
11    the same way as in Example 1, except that the catalyst  
12    was replaced by a commercial copper oxide catalyst for  
13    alcohol dehydrogenation (CuO: 70%/diatomaceous earth,  
14    specific surface area: 171 m<sup>2</sup>/g) which had been crushed  
15    to 20 to 40 mesh prior to use. The results are shown  
16    in Table 1.

17           As Table 1 shows, zinc oxide exhibits very  
18    low activity when used alone and a copper oxide cata-  
19    lyst becomes considerably deactivated with time, where-  
20    as the catalyst of this invention is superior in activ-  
21    ity and keeps up the high activity for a long time.

22    Example 2

23           A catalyst containing 2% of ruthenium was  
24    prepared in the same way as in Example 1, except that  
25    the zinc oxide was replaced by commercial magnesium  
26    oxide (MgO: 98%, specific surface area: 15 m<sup>2</sup>/g) which  
27    had been crushed to 20 to 40 mesh prior to use.

28           With this catalyst, the dehydrogenation reac-  
29    tion was carried out in the same way as in Example 1.  
30    The results are shown in Table 2.

31    Example 3

32           Magnesium oxide powder (20 to 40 mesh) as  
33    used in Example 2 was steeped in an aqueous solution of  
34    sodium carbonate prepared by dissolving a predetermined  
35    quantity of sodium carbonate in water. After standing  
36    for 1 hour, the solution was evaporated to dryness,



1 followed by drying in an oven at 120°C for 12 hours. The  
2 resulting product was then calcined in a muffle furnace at  
3 400°C for 1 hour. The resulting magnesium oxide containing  
4 3.3% of sodium carbonate was used as a carrier. Thus a  
5 catalyst containing 2% of ruthenium was prepared in the same  
6 way as in Example 1.

7 With this catalyst, dehydrogenation of 2-butanol  
8 was carried out in the same way as in Example 1. The results  
9 are shown in Table 2.

10 Table 2

11	12	13	14	15	16
	Example		Reaction		
	No.	Catalyst	Temperature	MEK Yield	MEK
			(°C)	(mol%)	Selectivity
					(mol%)
14	Example 2	Ru/MgO	250	19	97
15	Example 3	Ru/MgO-	250	21	99
16		Na <sub>2</sub> CO <sub>3</sub>			

17 Note: Reaction pressure: 10 kg/cm<sup>2</sup>G, LHSV (hr<sup>-1</sup>): 8,  
18 and reaction time: 100 hours.

1    Example 4

2            Ruthenium (1%)-zinc oxide catalyst was pre-  
3    pared in the same way as in Example 1. Without dilu-  
4    tion with quartz chips, the catalyst (9cc) was intro-  
5    duced into a stainless steel reactor tube, 20 mm in  
6    inside diameter. 2-Butanol was passed through the  
7    reactor tube at normal pressure and at an LHSV of 2  
8    hr<sup>-1</sup>. Table 3 shows the results obtained 2 hours  
9    after the start of the reaction.

10   Comparative Example 4

11            A rhodium (1%)-zinc oxide catalyst was pre-  
12    pared in the same way as in Example 1, except that  
13    ruthenium chloride was replaced by rhodium chloride.

14            With this catalyst, dehydrogenation reaction  
15    was carried out in the same way as in Example 4. The  
16    results are shown in Table 3.

17   Comparative Examples 5 and 6

18            An iridium (1%)-zinc oxide catalyst and a  
19    platinum (1%)-zinc oxide catalyst were prepared in the  
20    same way as in Example 1, except that ruthenium chlor-  
21    ide was replaced by chloroiridinic acid and chloro-  
22    platinic acid, respectively.

23            With these catalysts, the dehydrogenation  
24    reaction was carried out in the same way as in Example  
25    4. The results are shown in Table 3.

26   Comparative Example 7

27            A palladium (1%)-zinc oxide catalyst was  
28    prepared in the same way as in Example 1, except that  
29    palladium chloride was dissolved in a mixture of con-  
30    centrated hydrochloric acid (2 vol) and acetone (8 vol)  
31    instead of dissolving ruthenium chloride in acetone.

32            With this catalyst, the dehydrogenation reac-  
33    tion was carried out in the same way as in Example 4.  
34    The results are shown in Table 3.

1 Comparative Example 8

2 A silver (1%)-zinc oxide catalyst was pre-  
 3 pared in the same way as in Example 1, except that the  
 4 acetone solution of ruthenium chloride was replaced by  
 5 an aqueous solution of silver nitrate.

6 With this catalyst, the dehydrogenation reac-  
 7 tion was carried out in the same way as in Example 4.  
 8 The results are shown in Table 3.

9  
 10

Table 3

11	Example		Reaction		MEK selec-
12	No.	Catalyst	temperature	MEK yield	tivity
13			(°C)	(mol%)	(mol%)
14	Example 4	Ru/ZnO	200	20	100
15			250	72	100
16	Comparative	Rh/ZnO	200	10	95
17	Example 4		250	32	71
18					
19	Comparative	Ir/ZnO	200	2	67
20	Example 5		250	8	37
21	Comparative	Pt/ZnO	200	2	53
22	Example 6		250	5	15
23					
24	Comparative	Pd/ZnO	200	1	10
25	Example 7		250	6	26
26					
27	Comparative	Ag/ZnO	200	1	30
28	Example 8		250	2	17

2 A catalyst containing 5% of ruthenium was  
3 produced in the same way as in Example 1, except that  
4 zinc oxide was replaced by activated carbon (20 to 40  
5 mesh) which had been treated with 15% nitric acid under  
6 reflux for 6 hours.

11 Table 4

12		MEK Yield	MEK selec-
13	<u>Reaction time</u>	<u>(mol%)</u>	<u>tivity (mol%)</u>
14	After 2 hr	22	92
15	After 30 hr	15	95

19 Example 6

20 Ruthenium (1%)-magnesium oxide catalyst was  
21 prepared in the same way as in Example 2. Without  
22 dilution with quartz chips, the catalyst (9 cc) was  
23 placed in a stainless steel reactor tube, 20 mm in  
24 inside diameter. 2-Propanol was passed through the  
25 reactor tube under normal pressure, at 250°C, and at an  
26 LHSV of 2 hr<sup>-1</sup>. Thirty hours after the start of the  
27 reaction, acetone was obtained in a yield of 88 mol%.

CLAIMS

1. A process for producing a carbonyl compound which comprises dehydrogenating a linear aliphatic alcohol of 1 to 6 carbon atoms in the gas phase in the presence of a ruthenium catalyst supported on a carrier.
2. The process according to claim 1, in which the alcohol is secondary butanol and the carbonyl compound produced is methyl ethyl ketone.
3. The process according to claim 1 or 2, in which the dehydrogenation is carried out at a temperature in the range of 200°C to 250°C.
4. The process according to any of claims 1 to 3, in which the carrier comprises zinc oxide, magnesium oxide, calcium oxide or barium oxide.
5. The process according to claim 4, in which the carrier comprises zinc oxide or magnesium oxide with or without a minor amount of sodium carbonate.
6. The process according to any of claims 1 to 5, in which the ruthenium catalyst is reduced before use.
7. The process according to any of claims 1 to 6, in which the carrier supports 0.01 to 10 wt% ruthenium.
8. The use of a ruthenium catalyst supported on a carrier comprising zinc oxide or magnesium oxide in a process for producing a carbonyl compound which comprises dehydrogenating a linear aliphatic alcohol of 1 to 6 carbon atoms in the gas phase at a temperature in the range of 200°C to 250°C.

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9. The use according to claim 8 in which the alcohol is 2-propanol or 2-butanol and the carbonyl compound produced is acetone or methyl ethyl ketone, respectively.